

Decolorization of Rhodamine B by a Photo-Fenton Process: Effect of System Parameters and Kinetic Study

Y. S. Ma¹, C. N. Chang², C. R. Chao²

¹Department of Environmental Engineering and Health, Yuanpei University, Hsinchu, Taiwan

²Department of Environmental Science and Engineering, Tunghai University, Taichung, Taiwan

Email: ysma0728@mail.ypu.edu.tw

Abstract

A low-energy photo-Fenton process is carried out in this study to investigate the effect of pH, temperature, Fe^{2+} and H_2O_2 dosages on the decolorization of Rhodamine B dyeing wastewater. Experimental results indicate that the decolorization efficiency of Rhodamine B by UV light illumination only and UV/ H_2O_2 (H_2O_2 of 30 to 90 mg/L) are insufficient. Decolorization efficiency is remarkably enhanced to more than 83% by the photo-Fenton process at pH 5.5 and the pseudo first-order kinetic rate constants are in the range of $13.6\text{-}14.7 \times 10^{-3} \text{ min}^{-1}$. The optimal reaction condition is found at pH 3, H_2O_2 30 mg/L; Fe^{2+} 8 mg/L and 30°C followed by 98.3% decolorized efficiency of Rhodamine B. In conclusion, the photo-Fenton process can effectively decolorize the Rhodamine B in short reaction time under proper condition. Additional H_2O_2 and Fe^{2+} dosages and the reaction temperature up to 30°C are worthless to enhance the decolorization of Rhodamine B.

Keywords

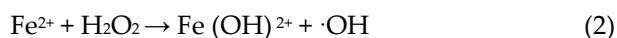
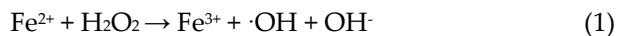
Decolorization; Photo-Fenton Process; Pseudo First-order Kinetic; Rate Constants; Rhodamine B

Introduction

Advanced oxidation processes (AOPs) have been generally employed as an attractive alternative method for the removal of hazardous, bio-refractory and toxic materials from waters and wastewaters. In principle, AOPs are known to generate highly reactive and non-selective hydroxyl radicals ($\cdot\text{OH}$), which is able to oxidize almost all toxic and non-biodegradable organic compounds to simple ones. AOPs, including ultra-violet (UV) illumination, ultrasound, ozonation, Fenton process and combinations thereof can efficiently produce

$\cdot\text{OH}$ to oxidize the pollutants and reduce the toxicity [1-4].

Photo-Fenton (UV light or visible light + Fenton) is a novel method in which water molecules undergo molecular fragmentation and release $\cdot\text{OH}$ to oxidize the organic compounds [5-7]. Generally, the most important advantage of photo-Fenton process is easier handling technologies without complex experimental apparatus. The most important reason that the photo-Fenton process can be effectively used in wastewater treatment is the synergistic effect by the coupled Fenton's reagent and UV illumination. Eq.1 shows the well-known Fenton reaction in solution. In this equation, Fe^{2+} is rapidly transferred to Fe^{3+} and produce $\cdot\text{OH}$. Recent reports indicate that the acceleration for decomposition of organic compounds is believed to be in order to photolysis of iron aqua complex, $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ (represented hereafter by $\text{Fe}(\text{OH})^{2+}$), to providing a new importance source of $\cdot\text{OH}$. Further, the photolysis of $\text{Fe}(\text{OH})^{2+}$ regenerates Fe^{2+} (Eqs.2 and 3), which means that the photo-Fenton reaction would need low Fe^{2+} concentration compared with the Fenton process [8]. This UV illumination isolated Fe^{2+} can react subsequently with H_2O_2 and produce $\cdot\text{OH}$ again (Eq. 1), and then a cyclic mechanism is established [9-12]. In addition, H_2O_2 can be isolated to two OH radicals by UV irradiation [13]; therefore, a photo-Fenton process has been proven as a profitable method for destroying and oxidizing the refractory compounds.



* Decolorization of Rhodamine B by a photo-Fenton

Rhodamine B is a typical fluorescent dye used as an ion-association reagent in solvent extraction photometry of anionic species and frequently used as fluorescence standard for absolute fluorescence quantum yield. It is also used extensively in biotechnology applications such as fluorescence microscopy, flow cytometry and fluorescence correlation spectroscopy. This cationic dye with an acid side chain, a well-known stable and non-volatile dye, has comparatively high resistance to photo and oxidation degradation. It is understood that the Rhodamine B will permeate into the human skin and cause the toxicity to human beings. Hence, if high concentration Rhodamine B presents in wastewater, a profitable degradation process is necessary to reduce the harmful effect to environment and human beings, based on the possible carcinogenic and toxicity of dyeing wastewater. Many researchers have tried to investigate the behaviors of Rhodamine B [14] and removal of this dye by activated carbon [15], ultrasound [16], visible-light with Nano-sized Bi_2WO_6 [17], graphite tailing/ H_2O_2 [18], fly ash sorption with Fenton pre-oxidation [19] and Fenton-like oxidation [20]. Besides the above methods, the UV illumination coupled with H_2O_2 [21], microwave [22], TiO_2 [23,24], ZnO [25], Fe-carbonnanotubes on TiO_2 [26], Fe^{0} -based Fenton [27] have also been carried out in these years to remove the Rhodamine B from aqueous phase.

In this study, a low-energy cost UV light carried out with applicable additions of chemicals such as Fe^{2+} and H_2O_2 are considered in this study for the treatment of Rhodamine B wastewater. The objectives of this study are to investigate the effect of reaction parameters such as Fe^{2+} and H_2O_2 dosages, pH and temperature on the decolorization of Rhodamine B dyeing wastewater and to investigate the Rhodamine B decolorization reaction kinetics by the pseudo first-order model in photo-Fenton system to find out the better reaction conditions.

Materials and Methods

Materials

Rhodamine B (purity > 89%, molecular weight = 1,017.65) was obtained from Sigma-Aldrich and the molecular structure of this dye has been shown [18, 19]. The chemical reagents used in this study also included ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, purity > 99.5%, Merck) and an aqueous solution of hydrogen peroxide (H_2O_2 ,

30% w/w in water, FERAK). These chemicals were the purest grade commercially available and were used without further purification. The stock Rhodamine B solution with 1,000 mg/L was prepared by dissolving the Rhodamine B powder in distilled and deionized water then stored in brown bottle at 4°C.

Maintaining the Integrity of the Specifications

A schematic drawing of the reactor is shown in Figure 1. A 1.6 L double-walled Pyrex glass reactor (working volume = 1 L) equipped with pH meter and oxidation reduction potential (ORP) meter (Suntex PC-3200, Taiwan) was with made for the experimental work. A temperature controller was used to maintain the reaction temperature in certain levels. Complete mixing of solution was achieved by a magnetic mixer with 100 rpm. Two 8-Watts monochromatic UV lamps of 312 nm (with emission range between 280 nm and 360 nm) were placed axially in the reactor and kept in place with a quartz sleeve; the UV intensity of each 8 Watts UV lamp was 60mW cm^{-2} . The value of the initial pH in all experiments including 3, 4, 5.5 and 7 were attained by adding 1N H_2SO_4 or NaOH as required without any buffer solution. During the reactions, the pH values varied freely without any hand correction. The Rhodamine B concentration was initiated at 20 mg/L. The UV lamp was warmed up for 30 minutes and the reactor was loaded with 1,000 mL Rhodamine B solution and designed dosages of Fe^{2+} (0, 4, 8 and 12 mg/L) and H_2O_2 (30, 60 and 90 mg/L) then mixed thoroughly to mark the start point of the experiment. The temperature was maintained at 15, 20, 30, 40 and 50°C, respectively, during the reaction. Reaction sets were sampled periodically (0, 2, 5, 10, 20, 30, 45 and 60 minutes) for analyses.

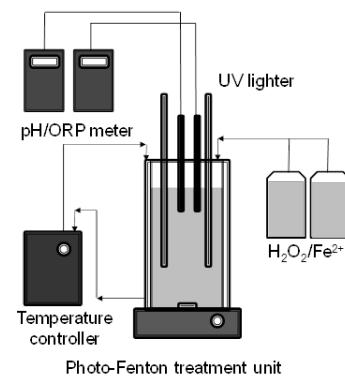


FIGURE 1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS DESIGNED FOR RHODAMINE B DECOLORIZATION

Analytic methods

The profiles of pH and ORP values were measured and recorded by pH and ORP meters. Rhodamine B in the samples was filtrated ($0.45\text{ }\mu\text{m}$) and analyzed by the spectrophotometer (UV-2102, Unico TM, USA) equipped with quartz cell at the wave length of 550 nm, where the absorption at the wavelength of 550 nm was named as A_{550} . The American Dye Manufacture Index (ADMI) was determined by measuring the transmittance at 590, 540 and 438 nm; the transmittance was converted to Tristimulus Value and Munsell Values to obtain the ADMI of the wastewater sample. The designed H_2O_2 concentration was measured by KI titration method.

Results and Discussion

Decolorization of Rhodamine B

In this study, the profiles of pH and ORP values during the decolorization of Rhodamine B were measured in all experiments. In Figure 2, the experiments were carried out at Rhodamine B concentration of 20 mg/L, pH 5.5, temperature of 20°C, H_2O_2 of 30 mg/L and Fe^{2+} of 0, 4, 8, 12 mg/L, respectively. Experimental results indicate that the pH values are decreased from 5.5 (before reaction) to 3.9 and 3.6 (after 60 mins reaction) at Fe^{2+} concentrations of 4 mg/L and 12 mg/L, respectively, and the difference of final pH values among different Fe^{2+} concentrations are insignificant (data were not shown). As it is observed, the initial ORP values of those experiments is 210 mV and then apparent increases when the H_2O_2 and Fe^{2+} are dosing and a slight increase with H_2O_2 dosing only. As can be seen, the maximum ORP values around 529.8 – 574.8 mV are taking place at the reaction time of 2 mins with Fe^{2+} of 4 – 12 mg/L addition and a progressive decrease is appreciated with reaction time. As the experiment was carried out without Fe^{2+} , the ORP values generally increased and kept constant after the reaction time of 20 mins. The differences of ORP values among the experiments with and without Fe^{2+} were in the range of 161.7 – 187.4 mV (reaction time of 60 mins), where the higher ORP values could be explained by the reaction between Fe^{2+} and H_2O_2 , named as the Fenton reaction.

A synergistic effect of UV irradiation and Fenton's reagent on the decolorization of Rhodamine B can be observed in Figure 3. This figure shows the results of Rhodamine B decolorization efficiency, based on the

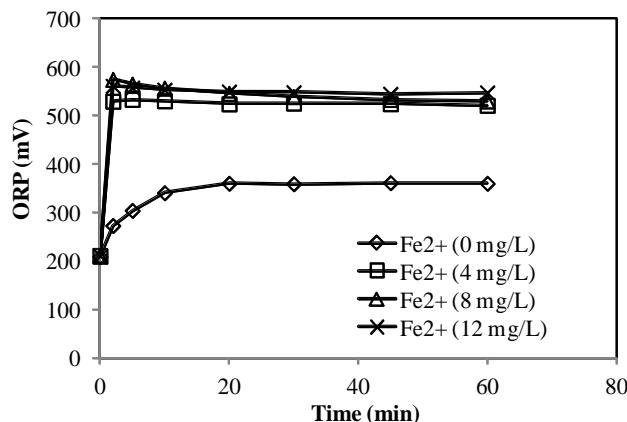


FIGURE 2 ORP PROFILES IN RHODAMINE B DECOLORIZATION BY PHOTO-FENTON PROCESS (H_2O_2 30 MG/L)

analysis of A_{550} , by photo-Fenton process. Decolorization efficiency was less than 5% without Fe^{2+} dosage, which indicated that the Rhodamine B was difficultly decomposed or decolorized by the UV/ H_2O_2 process. As the Fe^{2+} dosages increased to 4 mg/L, A_{550} was remarkably decreased from 2.094 to 0.983 with 10 mins reaction and continuously decreased to 0.784 and 0.563 within 20 and 60 mins reaction, where the maximum decolorization efficiency was 73.2%. When the Fe^{2+} increased to 8 and 12 mg/L, decolorization efficiencies were as high as 79.3% and 67.4%, respectively. This indicates that a synergistic effect between Fenton's reagent and UV light takes place in the decolorization system so that the Rhodamine B was significantly decolorized. However, it was also found in Figure 3 that the decolorization efficiency at Fe^{2+} of 12 mg/L was slightly lower than those of 4 and 8 mg/L. This phenomenon indicates that additional Fe^{2+} dosages can't provide sufficient oxidation potential in photo-Fenton system. As a result of iron photo-redox reaction and formation of hydroxyl radicals proposed by [28], the 2,4-dichlorophenol (DCP) elimination increased by increasing the initial Fe^{2+} concentration up to 45 mg/L, and, at the concentrations of Fe^{2+} higher than 45 mg/L, the DCP degradation efficiency decreased. Katsumata [8] found that the percent decrease of absorbance for humic acids (HA) in UV light at 254 nm and visible light at 400 nm rapidly increased with increasing initial Fe^{2+} concentration up to 1×10^{-5} mol/L. A small amount of brown condensate of iron and HA was

observed to be suspended in the solution during the photo-Fenton process when Fe^{2+} initial concentration was 1.5×10^{-5} mol/L so that the additional dosages of Fe^{2+} would inhibit the oxidation efficiency.

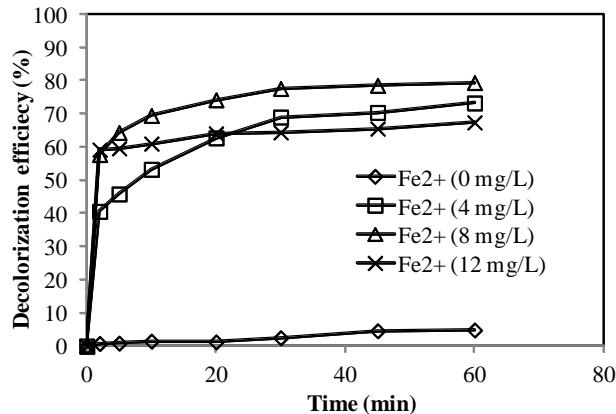


FIGURE 3 THE PROFILES OF RHODAMINE B DECOLORIZATION BY PHOTO-FENTON PROCESS (H_2O_2 30 MG/L)

Effect of H_2O_2 and Fe^{2+} dosages

It is well known that the dose of H_2O_2 is a key parameter in the Fenton, Fenton-like and photo-Fenton reactions. In this study, the effects of H_2O_2 and Fe^{2+} dosages on the decolorization efficiencies of Rhodamine B were also investigated to observe the better reaction conditions. Figure 4 shows the comparison of profiles of Rhodamine B decolorization efficiencies under different H_2O_2 (30 – 90 mg/L) and Fe^{2+} (0 – 12 mg/L) dosages with 60 mins reactions. As illustrated in Figure 4, decolorization efficiencies of Rhodamine B at different H_2O_2 dosages without Fe^{2+} are comparable (in the range of 4.2% - 4.9%), which indicates that the experiments carried out with UV/ H_2O_2 for Rhodamine B decolorization is insignificant. This is contrast to the results proposed as in [21], where the wavelength of UV lamp was selected as 254 nm and was effective to irradiate H_2O_2 to $\cdot\text{OH}$ to oxidize the organic compounds. In this study, the UV wave length was 312 nm, this could be explained by the slower $\cdot\text{OH}$ production rate in UV/ H_2O_2 system. Effect of Fenton oxidation on color removal of Rhodamine B was assessed by other studies. Chang [19] tried to treat the Rhodamine B (initial concentration of 100 mg/L) with Fenton method ($\text{H}_2\text{O}_2:\text{Fe}^{2+}$ molar ratio of 10:1) and found that 42% color removal was obtained after 30 min reaction while H_2O_2 of 1.5×10^{-3} M was used. When the H_2O_2 dose increased to 3×10^{-3} M, 95% of color removal was rapidly obtained at 2 min; however, the difference of

color removal with much more H_2O_2 dosages was insignificant, which indicated that additional H_2O_2 dosages were insufficient to remarkably enhance the decolorization efficiency for Rhodamine B. Hou [27] used Fe^0 and H_2O_2 at the initial pH 4.0 to decolorize the Rhodamine B and found that the degradation rate of Rhodamine B increased with the increase of H_2O_2 dose up to 0.80 mM and then decreased with H_2O_2 dose over 0.80 mM. The facts observed in [19] and [27] are comparable to this study.

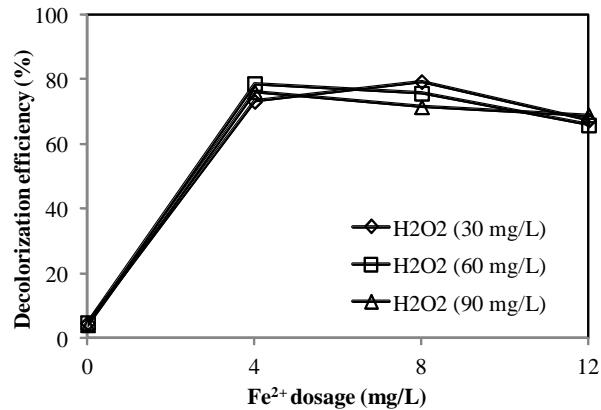


FIGURE 4 COMPARISON OF RHODAMINE B DECOLORIZATION AT DIFFERENT H_2O_2 AND Fe^{2+} DOSAGES

As it is observed, there is an increase in the decolorization of the Rhodamine B when the Fe^{2+} is dosing in this study. The decolorization efficiencies of Rhodamine B apparently increased to 73.2% - 78.7% as 4 mg/L Fe^{2+} and 30 – 90 mg/L H_2O_2 were dosing into the reactor, which were much higher than those of UV/ H_2O_2 process. As the Fe^{2+} increased to 8 and 12 mg/L, decolorization efficiencies of Rhodamine B were in the range of 71.5% - 79.3% and 65.9% - 69.0%, respectively. This phenomenon indicated that 4 or 8 mg/L of Fe^{2+} for the decolorization of 20 mg/L Rhodamine B were better than that of 12 mg/L Fe^{2+} . The highest decolorization efficiencies (79.3%) of Rhodamine B in Figure 4 took place at 30 mg/L of H_2O_2 and 8 mg/L of Fe^{2+} . Katsumata[8] showed the effect of initial H_2O_2 concentration on the removal of HA with the use of photo-Fenton process. The percent decrease of absorbance for HA increased with increasing the concentration of H_2O_2 added. Additional H_2O_2 did not drastically improve the maximum removal percentage. This would be due to self-decomposition of H_2O_2 to oxygen and water, and the recombination of $\cdot\text{OH}$ radical. Since $\cdot\text{OH}$ radical reacts with H_2O_2 , H_2O_2 itself contributes to the $\cdot\text{OH}$ radical

scavenger. Hence, additional dosages of oxidant or Fenton's reagent are worthless to enhance the decolorization of Rhodamine B in photo-Fenton system.

Effect of temperatures and pH levels

Not only the effect of Fenton's reagent dosages but also the reaction temperatures and pH levels on the degradation or oxidation of dyeing wastewater and organic compounds have been studied in many researchers [4,5,9]. It is understood that the temperatures of most real industrial wastewater are varied in different industries hence the effect of temperature on Rhodamine B decolorization are important and is investigated in this study. Figure 5(a) shows the results of Rhodamine B decolorization at temperatures of 15, 20, 30, 40 and 50°C where the H_2O_2 and Fe^{2+} dosages are 30 and 8 mg/L.

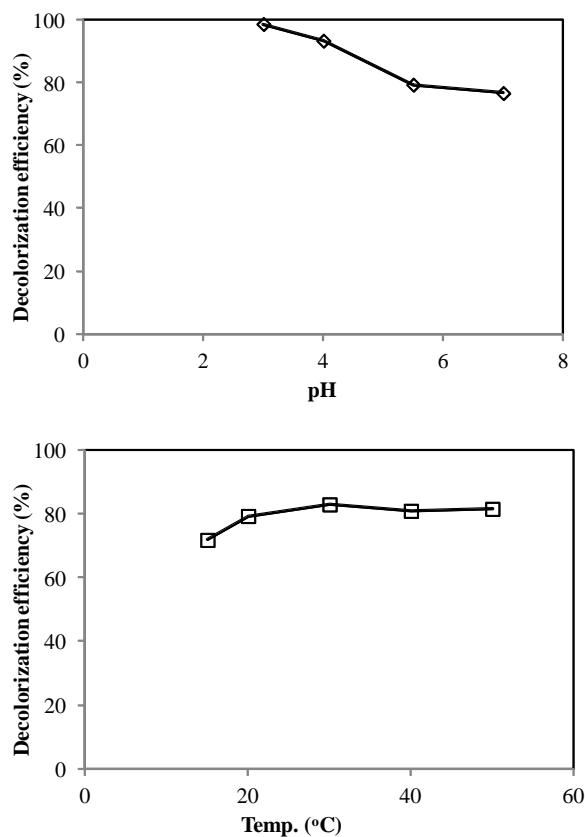


FIGURE 5. COMPARISON OF RHODAMINE B DECOLORIZATION AT (A) DIFFERENT TEMPERATURES (B) DIFFERENT pH LEVELS (H_2O_2 AND Fe^{2+} DOSAGES OF 30 AND 8 MG/L).

Experimental results show that the decolorization efficiency was 71.8% at 15°C within 60 min reaction and increased to 79.3%, 83.0%, 81.0%, 81.6% when the

reaction temperatures increased to 20, 30, 40 and 50°C, respectively. This fact indicates that higher the reaction temperatures higher the decolorization efficiencies; also, as the temperature is increased to more than 30°C, a slightly decrease in Rhodamine B decolorization takes place. Pérez[5] also tested the effect of reaction temperature (25, 40 and 70°C) on the oxidation of textile effluents by Fenton and photo-Fenton processes. It was found that the temperatures above 25°C and up to 70°C showed a beneficial effect on organic load reduction. Torrades[9] investigated that effect of Fe^{2+} and H_2O_2 initial concentration, and temperature on the treatment of cellulose bleaching effluents. It was found that the treatment efficiency of cellulose bleaching effluents at 30°C and 70°C were to be similar. Hence, temperature had an important effect in the organic matter degradation, especially when the ratio of Fenton reagents was not properly chosen [9]. That is, based on the results shown in literatures and this study, a high reaction temperature might not be a key reaction parameter in photo-Fenton system for dyeing or textile wastewater treatment. Figure 5(b) shows the effect of pH on the decolorization efficiency of Rhodamine B by the photo-Fenton process, where the initial pH levels are 3, 4, 5.5 and 7 where the H_2O_2 and Fe^{2+} dosages are also 30 and 8 mg/L. Decolorization efficiency of Rhodamine B after 60 min reaction was only 76.7% at pH 7, and increased to 79.3%, 93.4% and 98.7% as the pH levels decreased to 5.5, 4 and 3, respectively. This result indicates that the lower pH levels would be beneficial to get the better decolorization efficiency in photo-Fenton system. Chang[19] also proposed the comparable results. As the Fenton method was used to decolorize the Rhodamine B at pH 2, 3, 4 and 5, higher Rhodamine B color removal (>90%) was obtained at pH 2–3 than that (66%) at pH 4–5 after 30 min reaction time. AlHamed[21] used the UV/ H_2O_2 process to decolorize the Rhodamine B and investigated the effect of pH levels (1, 7 and 9) on the decolorization efficiency. It was found that pH 7 showed the better decolorization efficiency than pH 1 and pH 9. Therefore, concerning the results shown in [21] and this study, if the photo-Fenton process is only used as a pretreatment method and a bioreactor will be connected as a following treatment unit, the reaction pH levels of 5.5 and pH 7 still can provide satisfactory decolorization

efficiencies for Rhodamine B dyeing wastewater.

Discussion

From Figure 3 to Figure 5, the decolorization efficiency were obtained by the measurement of UV light absorbance at the wavelength of 550 nm, named as A_{550} , to point out the degradation of Rhodamine B. During the experiments, the authors also checked the profiles of ADMI so that the standardization data of dyeing wastewater treatment could be observed in this study. As can be seen in Figure 6, the profile curves of A_{550} and ADMI at H_2O_2 30 mg/L without Fe^{2+} are comparable; after 60 mins reaction, reduction of A_{550} and ADMI are 4.8% and 3.9%, respectively. When the Fe^{2+} increased to 8 mg/L, the profile curves of A_{550} and ADMI are different. After 60 mins reaction, reduction of A_{550} is 79.3% and ADMI is 92.6%; this higher ADMI reduction result indicates that the degraded Rhodamine B would be oxidized or transferred to other intermediates in aqueous phase and these intermediates are simultaneously degraded by photo-Fenton system.

Table 1 shows the results of Rhodamine B decolorization efficiencies, H_2O_2 usage and their pseudo first-order rate constants at different reaction conditions by sole UV light, Fenton process and photo-Fenton process. The very low decolorization efficiencies and rate constant were found at the experiments carried out with UV light only. After 60 mins reaction, decolorization efficiencies were only 0.3% and 1.0% where 0 mg/L and 8 mg/L of Fe^{2+} was dosing into the system. In Fenton system (H_2O_2 of 30 mg/L), decolorization efficiencies were 2.6%, 63.5%, 75.8% and 68.5% where the Fe^{2+} dosages were 0 – 12 mg/L, respectively. When the UV light was coupled with Fenton process, decolorization efficiencies were 4.8%, 73.2%, 79.3% and 67.4%, respectively. The higher decolorization efficiencies in photo-Fenton system proved that the synergistic effect of UV irradiation and Fenton's reagent is available in the dyeing wastewater treatment. However, slightly decolorized enhancement of Rhodamine B in photo-Fenton system was observed at Fe^{2+} of 8 mg/L (75.8% of Fenton system and 79.3% of photo-Fenton system). Lucas and Peres (2006) found that the azo dye Reactive Black 5 could be effectively decolorized using Fenton and photo-Fenton processes with a little difference between the two processes, 97.5% and 98.1%, respectively, for optimal conditions. This fact indicates that UV low-pressure mercury lamp might

have little effect on dye decolorization.

TABLE 1 COMPARISON OF RHODAMINE B DECOLORIZATION AND THEIR PSEUDO FIRST-ORDER RATE CONSTANT AT DIFFERENT REACTION CONDITIONS (H_2O_2 OF 30 MG/L)

Item		Decolorization efficiency (%)	H_2O_2 usage ^a	k^b	R^2
UV only	[Fe^{2+}] ^a				
	0	0.3	-	-	-
Fenton	8	1.0	-	0.1	0.92
	0	2.6	3.6	0.3	0.93
	4	63.5	8.5	7.7	0.94
	8	75.8	17.0	10.5	0.91
Photo-Fenton	12	68.5	10.1	3.6	0.93
	0	4.8	5.1	0.8	0.93
	4	73.2	12.1	11.4	0.89
	8	79.3	21.0	13.6	0.92
	12	67.4	12.5	3.8	0.93

^aunit: mg/L; ^bunit: 10^{-3} min^{-1}

In addition, Table 1 also shows the H_2O_2 usages during the decolorization with different treatment methods. It was found that the usages of H_2O_2 for Fenton system increased from 3.6 to 17.0 mg/L (initial addition was 30 mg/L) since the Fe^{2+} were increased from 0 to 8 mg/L; this increase in H_2O_2 usage also led to the increase in decolorization efficiency. In photo-Fenton system, comparable results were observed, where the H_2O_2 usages were varying from 5.1 to 21.0 mg/L and the decolorization efficiencies were increased to as high as 79.3%. Comparing the results of Fenton and photo-Fenton systems, it was also found that the usage of H_2O_2 in photo-Fenton system were higher than Fenton system. This could be explained by the Eq. (3), where the intermediate ($Fe(OH)^{2+}$) is easily decomposed to Fe^{2+} and this produced Fe^{2+} would react with H_2O_2 hence the usage of H_2O_2 in photo-Fenton system is higher than Fenton system. This study also investigates the decolorization rate constants of Rhodamine B with pseudo first-order kinetic model, and the results are shown in Table 1. In Fenton system, the rate constant were in a range of $0.3 - 10.5 \times 10^{-3} \text{ min}^{-1}$, and the highest rate constant was taking place at the condition of 30

mg/L H₂O₂ and 8 mg/L Fe²⁺. Comparable results are observed in photo-Fenton system. At 8 mg/L Fe²⁺ condition, the rate constant was 13.6×10^{-3} min⁻¹, which was higher than other Fe²⁺ dosages. That is, the reaction condition of 8 mg/L Fe²⁺ shows the better decolorization efficiency and higher reaction rate constants. As the Fe²⁺ increases to 12 mg/L, both the decolorization efficiency of Rhodamine B and reaction rate constants were decreased. Therefore, higher Fenton's reagent dosages would be profitable to obtain the initially higher decolorization of Rhodamine B but worthless to extend the oxidation capacity for longer reaction period.

Conclusions

This study tried to apply the UV illumination, Fenton and photo-Fenton processes to treat the Rhodamine B dyeing wastewater and investigated the effect of experimental parameters on the decolorization of Rhodamine B; a pseudo first-order reaction kinetic model was used to simulate the reaction profiles of Rhodamine B decolorization and obtain the rate constant at different reaction conditions. It was found that less than 5% of Rhodamine B was decolorized by UV or UV/H₂O₂ process within 60 mins reaction, and remarkably increased to 65.9 to 79.3% by photo-Fenton process at pH 5.5. The maximum Rhodamine B decolorization efficiency reached 98.3% as the pH decreased to 3 with 30 mg/L H₂O₂ and 8 mg/L Fe²⁺. A synergistic effect of UV irradiation and Fenton's reagent on the decolorization of Rhodamine B could be observed in this study at the lower dosages of Fenton's reagent condition. Additional Fe²⁺ and H₂O₂ dosages were worthless on the enhancement of Rhodamine B decolorization. Effect of temperature on Rhodamine B decolorization was insignificant with properly dosages of Fenton's reagent.

ACKNOWLEDGEMENTS

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REFERENCES

- [1] H. Lee and M. Shoda, *J. Hazard. Mater.* 153, 1314 (2008).
- [2] Y. S. Ma and C. N. Chang, *Ozone-Sci. Eng.* 32, 265 (2010).
- [3] Y. S. Ma, C. F. Sung and J. G. Lin, *J. Hazard. Mater.* 178, 320 (2010).
- [4] L. A. Lu, Y. S. Ma, M. Kumar and J. G. Lin, *Chem. Eng. J.* 166, 150 (2011).
- [5] M. Pérez, F. Torrades, X. Domènec and J. Peral, *Wat. Res.* 36, 2703 (2002).
- [6] R. A. Torres, F. Abdelmalek, E. Combet, C. Petrier and C. Pulgarin, *J. Hazard. Mater.* B146, 546 (2007).
- [7] J. Liang, S. Komarov, N. Hayashi and E. Kasai, *Ultrason. Sonochem.* 14, 201 (2007).
- [8] H. Katsumata, M. Sada, S. Kaneko, T. Suzuki, K. Ohta and Y. Yobiko, *Chem. Eng. J.* 137, 225 (2008).
- [9] F. Torrades, S. Saiz, J. A. García-Hortal and J. García-Montaña, *Environ. Eng. Sci.* 25, 92 (2007).
- [10] H. S. Son, S. B. Choi, E. Khan and K. D. Zoh, *Wat. Res.* 40, 692 (2006).
- [11] M. R. A. Silva, A. G. Trov'o and R. F. P. Nogueira, *J. Photochem. Photobiol. A Chem.* 191, 187 (2007).
- [12] H. Zhang, J. Zhang, C. Zhang, F. Liu and D. Zhang, *Ultrason. Sonochem.* 16, 325 (2009).
- [13] A. K. De, B. Chaudhuri, S. Bhattacharjee and B. K. Dutta, *J. Hazard. Mater.* B64, 91 (1999).
- [14] T. Karstens and K. Kobs, *J. Phys. Chem.* 84, 1871 (1980).
- [15] K. Kadirvelu, C. Karthika, N. Vennilamani and S. Pattabhi, *Chemosphere* 60, 1009 (2005).
- [16] M. Sivakumar and A. B. Pandit, *Ultrason. Sonochem.* 8, 233 (2001).
- [17] H. Fu, C. Pan, W. Yao and Y. Zhu, *J. Phys. Chem. B* 109, 22432 (2005).
- [18] C. Bai, W. Gong, D. Feng, M. Xian, Q. Zhou, S. Chen, Z. Ge and Y. Zhou, *Chem. Eng. J.* 197, 306 (2012).
- [19] S. H. Chang, K. S. Wang, H. C. Li, M. Y. Wey and J. D. Chou, *J. Hazard. Mater.* 172, 1131 (2009).
- [20] X. Xue, K. Hanna and N. Deng, *J. Hazard. Mater.* 166, 407 (2009).
- [21] F. H. AlHamed, M. A. Rauf, S. S. Ashraf, *Desalination* 239, 159 (2009).
- [22] S. Horikoshi and H. Hidaka, *Environ. Sci. Technol.* 36, 1357 (2002).
- [23] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka and N. Serpone, *Environ. Sci. Technol.* 32, 2394 (1998).

- [24] R. Jain, M. Mathur, S. Sikarwar and A. Mittal, *J. Environ. Manage.* 85, 956 (2007).
- [25] K. Byrapa, A. K. Subramani, S. Ananda, K. M. L. Rai, R. Dinesh and M. Yoshimura, *Bull. Mater. Sci.* 29, 433 (2006).
- [26] K. Zhang, Z. Meng and W. OH, *Chin. J. Catal.* 31, 751 (2010).
- [27] M. F. Hou, L. Liao, W. D. Zhang, X. Y. Tang, H. F. Wan and G. C. Yin, *Chemosphere* 83, 1279 (2011).
- [28] F. A. Momani, C. Sans and S. Esplugas, *J. Hazard. Mater.* B107, 123 (2004).